Tutor/s

Dr. Jordi Ignés-Mullol
Departament de Ciència de Materials i Química Física

Grau de Química

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Preparation of glass surfaces with controlled liquid affinity and photosensitive wetting properties.

Preparació de superfícies de vidre amb afinitat controlada pels líquids i propietats de mullat fotosensibles.

Elba Guasch García

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"God made the bulk; the surface was invented by the devil".

Wolfgang Pauli

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REPORT

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1. SUMMARY

Many procedures relay on specific wetting properties. Surface functionalization is an effective mechanism by which surface properties can be modified, including wettability. It is well known that functionalization using silane self-assembled monolayers can change SiO_2 from hydrophilic to hydrophobic. We have studied three different mechanisms with which glass can be provided with specific water affinity: controlled monolayer degradation, deposition of short and long-chain alkylsilane mixtures and modification of the monolayer structures employing isomerization of photosensitive silanes . The study was carried out using contact angle measurements, ellipsometry and UV-Visible spectroscopy. It was demonstrated that with different molar fractions of varying chain-length alkylsilanes, different contact angle values can be obtained. Photosensitive glass slides also showed promising results as the wetting properties changed when isomerization was induced. The effect that the monolayer degradation has over wetting could not be proved due to lack of proper equipment.

Keywords: Wetting, self-assembly, surface functionalization, silanes, contact angle, glass, photosensitive.

2. RESUM

Molts procediments depenen de propietats específiques de mullat. La funcionalització de superfícies es un mecanisme efectiu pel qual diferents propietats d'una superfície es poden modificar, entre elles la mullabilitat. Se sap que la funcionalització mitjançant monocapes de silans auto assemblats pot fer canviar l'SiO_2 d'hidròfil a hidròfob. S'han estudiat tres mecanismes diferents amb què es pot dotar al vidre d'afinitat especifica envers l'aigua: degradació controlada de les monocapes, deposició de mescles d'alquilsilans amb cadenes de diferent llargada i modificació de l'estructura de les monocapes a partir de la isomerització de silans fotosensibles. L'estudi s'ha dut a terme mitjançant mesures d'angle de contacte, elipsometria i espectroscòpia UV-Vis. S'ha demostrat que es poden obtenir diferents angles de contacte a partir de diferents fraccions molars d'alquilsilans amb cadenes de llargada variable. Les làmines de vidre fotosensibles també han presentat resultats prometedors, ja que les propietats de mullat han canviat quan s'ha induït la isomerització. L'efecte que la degradació de les monocapes té sobre la mullabilitat no s'ha pogut confirmar per falta d'equipament adequat.

Paraules clau: Mullabilitat, auto assemblatge, funcionalització de superfícies, silans, angle de contacte, vidre, fotosensible.

3. INTRODUCTION

Many technologies depend on well-optimized wetting properties to ensure good performance. In oil recovery industries, materials that selectively absorb oil but not water are needed [1]; in medicine, high interaction with liquids and titanium implants allows for better bone-cell attachment, enabling better integration of the implant with the bone [2]; liquid crystal (LC) based biosensors rely on the wetting properties of the LC and the surface to maintain a uniform and stable film with the desired thickness [3], [4]. One effective way to modify wettability is through surface functionalization, in which specific molecular assemblies are formed over the surface.

This work is focused on the modification of glass surface wetting properties using surface functionalization. To further understand all the results some important concept are explained in the following sections.

3.1. WETTING PROPERTIES

Wettability is the ability of a liquid to maintain contact with a solid surface, and it is controlled by intermolecular forces between the liquid and the surface (adhesive) and within the same liquid (cohesive) [5].

In this section, the physical aspects of wetting properties will be described, as well as wetting characterization by contact angle measurements.

3.1.1. Surface free energy and surface tension

Intermolecular interactions are attractive or repulsive forces between neighbouring molecules that appear as a consequence of their electrical properties. Van del Waals forces and hydrogen bonds are some of the most important intermolecular forces [6].

Molecules attraction is responsible for the formation of condensed phases (liquid and solid), but as soon as they come into contact molecules repel each other. That is to say, intermolecular forces define bulk properties as molecules arrange themselves according to the attractive and repulsive forces to decrease the system energy.

A perfect gas has no intermolecular forces, so its molecules are completely disordered in the totality of the space. On the other hand, perfect crystals have high-ordered structures (long-range order) because of strong forces between molecules, atoms or ions. Liquids lie in the middle: a short-range order can be found in the bulk but its structure is very mobile. *Cohesive force* is the term used to describe intermolecular forces between molecules of the same substance, which are responsible for the union of liquid molecules [7].

As mentioned before, the structure of the liquids is mobile. This allows molecules enough movement to adopt shapes that maximizes the number of molecules in the bulk, stabilizing the structure of the liquid as there are more intermolecular interactions. Spheres are the shape with the smallest surface-to-volume ratio which explains why liquid droplets tend to be spherical. Some molecules always remain in the interface with lower interaction (Fig. 1). As attractive forces of molecules in the interface are not equal in all the directions, a neat force pulls them to the inside of the bulk: the *surface tension* (γ).

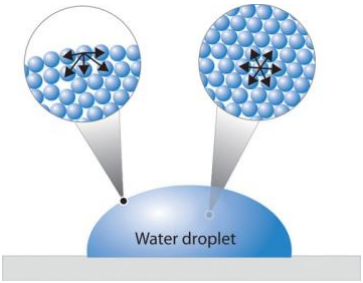


Fig. 1 Difference between bulk and the interface intermolecular. *CC BY-SA-NC.*

To further understand surface tension, imagine a cut made perpendicular to the surface of a body (liquid or solid). To maintain the same structure it is necessary to apply forces near the surface to compensate for the lack of intermolecular forces form the removed neighbour atoms. This surface stress can be balanced by either external forces (leading to surface atom rearrangement in solids) or volume stress in the material below the surface (hydrostatic pressure inside a drop in liquids) [8].

Another important concept is the *surface free energy*. In proper conditions, the external work (w) needed to modify the surface area (σ) can be equal to the increase in the total free energy of the system, so one can define surface free energy as the energy variation of a surface when the number of surface molecules varies. It can be written as:

$$dw = \gamma d\sigma \quad \text{Eq.1}$$

This expression (Eq.1) gives a thermodynamic explanation to surface tension, as it is the constant of proportionality (γ). Its units are energy/area, Jm^{-2} in SI. However, it is usually reported in $1Nm^{-1}$ ($1J = 1Nm$ so $1Jm^{-2} = 1Nm^{-1}$) [6].

In liquids, surface tension and surface free energy are numerically the same and sometimes this two concepts get confused. It is common to talk about the liquid surface tension, while in solids the surface free energy is used [8].

External forces can modify the ideal surface structure. In the case of liquids, gravity and interaction with other interfaces may distort the ideal spherical drop shape. *Adhesive forces* is the general term used to describe attractive intermolecular forces between different substrates. When adhesive forces between a liquid and a surface are strong enough liquid surface tension is reduced, pulling de drop out of its spherical formation and speeding it over the surface. [7]

If a liquid has a high affinity to the surface due to strong adhesive forces, it is said that the surface has high wettability towards that specific liquid. To modify wetting properties, molecules can be grafted into the surface to achieve an specific intermolecular attraction with the desired liquid. One method of surface modification is surface functionalization with self-assembly monolayers, which will be the main topic of this work.

3.1.2. Contact angle measurements

Wetting characterization is commonly carried out by the measurements of contact angle: the angle between the tangent to the liquid–vapour interface and the solid surface at the three-phase contact line (Fig. 2a) [9].

In 1805, Thomas Young defined the relationship between surface tension and contact angle [10]. For a liquid drop in equilibrium with its vapour phase on a solid surface, the contact angle is influenced by three interfacial forces: solid-vapour surface tension (γ_{SV}), solid-liquid surface tension (γ_{SL}) and liquid-vapour surface tension (γ_{LV}) (Fig. 2a). They can be related with the contact angle through Young's equation:

$$cos\theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad \text{Eq.2}$$

where θ_Y is the contact angle for an ideal surface: rigid, flat, non-reactive, inert, homogeneous, insoluble, smooth, and nonporous. These conditions are usually not met in real surfaces, so exact values of surface tension cannot be calculated from contact angle and the Eq.2.

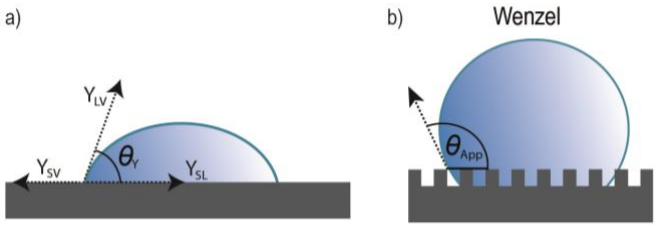


Fig. 2 Contact angle drop representation. a) Balanced surface tensions b) Wenzel model

The measured angle for surfaces is called the apparent contact angle θ_{app}, and it can be related to the Young contact angle (θ_Y) thought different models depending on the surface structure and composition [11].

In 1936 Robert N. Wenzel reported for the first time the importance of surface roughness. He proposed the equation

$$cos\theta_w = r\ cos\theta_Y \quad \text{Eq.3}$$

where the apparent contact angle (or Wenzel angle, θ_w) is related to Young's contact angle (θ_Y) through a roughness parameter(r). It was derived based on the assumption that the drop is big enough to completely penetrates surface cavities (Fig. 2b). He stated that by increasing surface per unit area, the wetting properties of the materials are enhanced, as more interactions in the solid-liquid interface take place [12].

Despite the lack of precision that contact angle measurements have when calculating surface tension, it can be considered effective when characterizing wetting properties of the surfaces:

- Contact angle < 90º: High wettability (the liquid wets the surface). It occurs when the solid has high surface free energy or there is low surface-tension in the liquid. ($\gamma_{SV} < \gamma_{LS}$). High adhesive forces.
- Contact angle > 90º: Low wettability (the liquid maintain its spherical structure). It occurs when the solid has low surface free energy or there is high surface-tension in the liquid ($\gamma_{SV} < \gamma_{LS.}$). The cohesive forces of the liquid are stronger than the surface-liquid interaction.

If the liquid at hand is water then the surface is considered hydrophobic when contact angle > 90º, and hydrophilic when contact angle > 90º. If contact angle is > 150º the surface is said to be super-hydrophobic [11].

S*essile-drop goniometry* is used in this work as contact angle measurement method. It is performed by taking photos of a water drop on a solid surface and determining the contact angle from the images by a fitting procedure [9]. The simplicity of the infrastructure is an advantage (Fig. 3), however the fittings are highly influenced by the assignment of the tangent line, so specific guidelines are needed for good accuracy and reproducibility of the results.

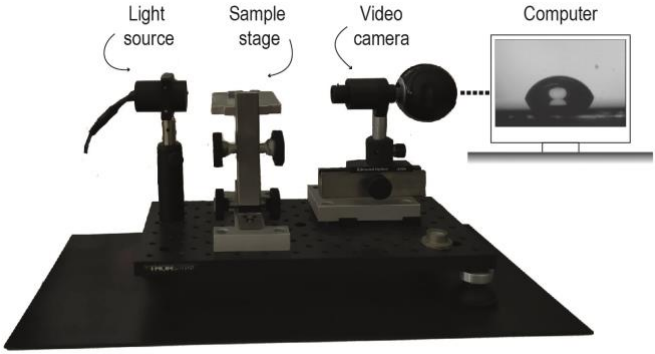


Fig. 3 Goniometer used in this work. A basic goniometer has a light source, an adjustable sample stage, a camera to record images and a computer for data analysis.

3.2. SELF-ASSEMBLED MONOLAYERS (SAMS)

Surface functionalization is an effective way in which the surface properties of materials can be modified without altering the properties of the bulk. This functionalization can be achieved through self-assembled monolayers (SAMs); ordered molecular assemblies formed by the spontaneous adsorption of an active surfactant onto the surface [13] (Fig. 4).

SAMs can be used to functionalize different types of surfaces, from thin metal films to nanoparticles, leading to a huge array of applications in many fields (surface coating, biosensors, catalysis …) [14].

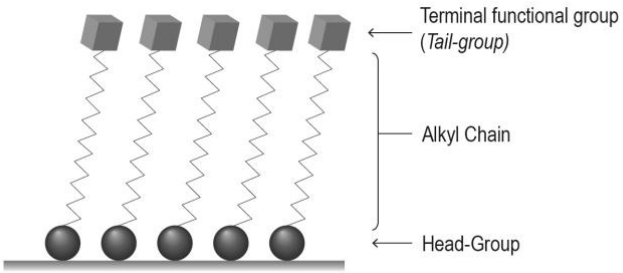


Fig. 4 Schematic diagram of an ideal SAM

The key of SAM is the selection of molecules with *head-groups* with specific affinity for the surface. Different headgroups with different affinities have been studied over the years [15]. Common SAMs include thiols on metals like gold, silver and copper; organosilanes on hydroxylated surfaces; and fatty acids on alumina The surfactant that forms the SAMs have a *tail-group,* which gives the surface its new specific properties [16]. It can also be used for further modification through nucleophilic substitution. For instance, reactions with peptide fragments with cysteine as nucleophiles lead to monolayer with these peptides on the surface [13].

This work is focused on functionalized glass with SAMs through salinization to modify its wetting properties.

3.2.1. Silanization mechanism

Organosilanes offer huge potential as SAMs because they can form monolayers on a wide variety of surfaces, such as silicon oxide, aluminium oxide, quartz, glass, mica, zinc selenide, germanium oxide, and gold [13].

The common preparation is by wet chemical processing, in which the previously-hydroxylated surfaces is immersed into diluted solutions of organosilanes, such as alkyltrichlorosilanes (X-(CH_2)n -$SiCl_3$; n > 3) or alkyltriethoxysilanes (X-(CH_2)n -Si- $(OCH_3)_3$; n > 3), usually in an organic solvent [17]. Despite many efforts, the exact details of the silanization mechanism remain nowadays unclear, making the obtention of high-quality SAMs challenging.

The most commonly accepted mechanism was described in 1980 [18]. Hydration water from the oxide surface [19] hydrolyses the silane to trisilanol. As a consequence, chains are bonded by hydrogen bonds to the surface -OH and to their close neighbours, generating an unstable situation that leads to water elimination (Fig. 5a). The result is a monolayer in which the molecules

are connected to each other (polysiloxane) and to the surface forming a network with strong Si—O—Si bonds [18].

Even though there is strong evidence for this mechanism in the case of trichlorosilanes, another mechanism have been proposed for trialkoxysilanes. It involves direct reaction of the alkoxy groups with surface hydroxyl via an addition–elimination type mechanism, without the formation of the trisilanol intermediate [20] (Fig. 5b).

The trialkoxysilanes mechanism was proposed after studying silanes with different with alkoxy group length. It was proved that silane surface density can be controlled by simply altering the size of the silane group, which should not happen if trisilanol is formed as an intermediate.

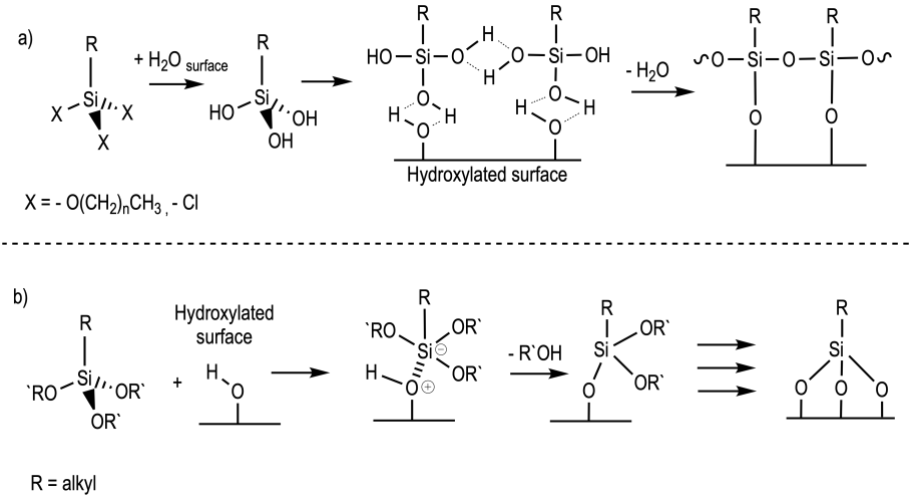


Fig. 5 a) Classical mechanism for the reaction of trichlorosilane b) Proposed addition–elimination mechanism for the reaction of trialkoxysilanes. (*Adapted from [20] with permission of The Royal Society of Chemistry)*

3.2.2. Surface structure

Different structures for the monolayers can be obtained with slight changes in the reaction conditions, so well-ordered assemblies are difficult to achieve. Even after many years of research where scientists have worked on identifying and optimizing the factors affecting silane monolayer formation, there are still some unclear peculiarities.

One of the main reasons for this lack of order is that the mobility of individual molecules is restricted by polymerization between neighbouring silanes, so redistribution of the molecules after

the absorption to obtain more stable arrangements does not take place. This polymerization does not happen in other SAMs such as fatty acids on AgO or thiols on gold [13].

Silane polymerization competes with the silane-surface reaction . Water content, temperature, nature of the silane, and type of substrate have been reported to influence which one of the two reactions take place and therefore defining the surface structure [21]. Incomplete monolayers are formed in absence of water, but water excess results in polymerization in solution [17], [22]. On the other hand, when temperature decreases the reaction with the surface is preferred. Moreover, with lower temperatures the reaction kinetics decreases and with it the thermal disorder in the forming monolayer, obtaining more ordered monolayers [23].

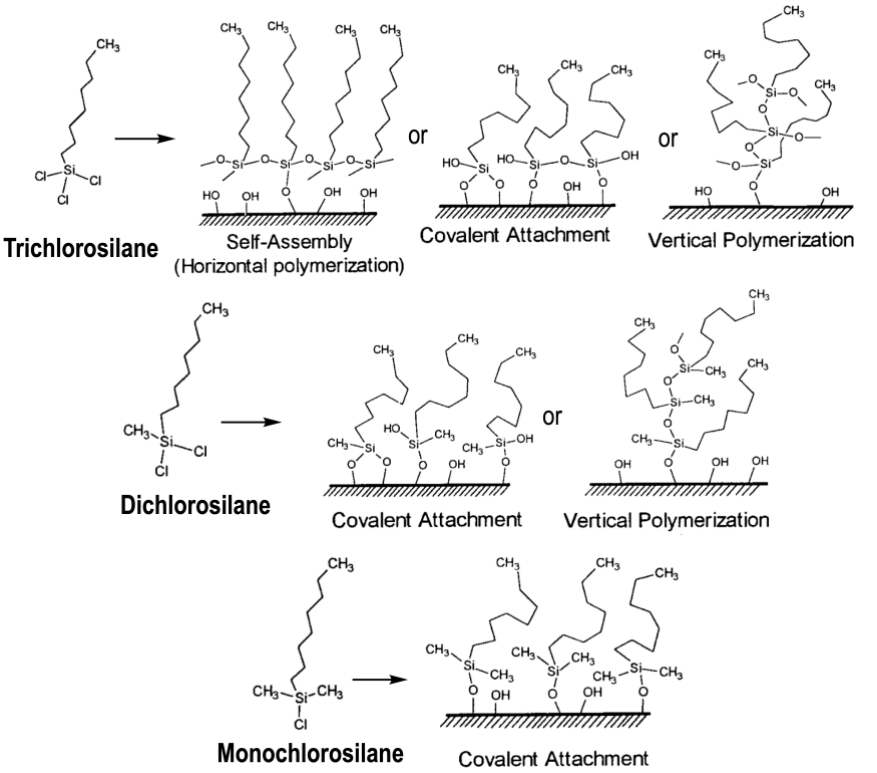


Fig. 6 Possible structures of the reaction of alkylchlorosilanes with hydroxylated SiO_2.. (Adapted with permission form [24]. Copyright 2021 American Chemical Society)

Trifunctional silanes ($RSiX_3$) can form multiple bonds with the surface and polymerize (lateral and vertical) with neighbouring silanes. Consequently, different reaction conditions can produce three different surface organizations: Self-assembly (SAM), covalent attachment and polymerization (Fig. 6).

SAMs are defined by lateral siloxane bonds, van der Waals interactions between *trans* alkyl chains and small bonding with the surface [24].

Covalent attachment, also known as poor self-assembly because its lower bonding density, occurs when alkyltrichlorosilanes react predominately with surface -OH. It has been described when adsorbed amine is present in the reaction media at room temperature [24] and for silanization of dry silica at elevated temperatures [22]. Ellipsometry analysis indicates that covalently attached monolayers are thinner than the fully stretched alkyl chain and SAM, so it is thought that alkyl chains are disordered [24].

If there is enough water in the reaction system, the condensation of trifunctional silanes (polimerization) is the dominant process, grafting 3-D siloxanes to the surface [24].

Monofunctional organosilanes (R_3SiX) just have one hydrolysable group (X =-OR, - Cl, $-NMe_2$) and can form a single Si-O-Si bond with the surface. In the case of difunctional organosilanes (R_2SiX_2), both covalent attachment and polymerization are possible (Fig. 6).

4. OBJECTIVES

Glass is a relatively cheap material with many different applications where specific liquid affinity might be needed in some cases. This work offers three different approaches towards glass wetting properties modification, in which surface functionalization with silanes is used.

Wetting properties change when silane monolayers degrade. It has been proved that different degradation degrees can be related to specific contact angles [4]. Exposure to UV light and plasma treatment (Appendix 1) were used as degradation mechanisms to study the relationship between degradation and water affinity.

It was published that alkylsilanes with different alkyl chain-length have different wetting properties [24]. In addition, recent works demonstrated that by mixing short and long altkylsilanes, one can obtain the desired liquid adhesion [3]. We characterized glass slides functionalized with

different mixtures of C2 and C18 alkylsilanes using contact angle measurements and ellipsometry data to further prove these results.

The “azo” compounds have the functional group R−N=N−R', in which R and R' can be either aryl or alkyl. This type of molecules are photosensitive and change for *trans* to *cis* isomer when absorbing UV light. Taking advantage of this property, photosensitive glass slides can be obtained when functionalized with silanes that have an azo group in its structure [25]. Using a mixture of a no-photosensitive and a custom-made photosensitive silane, we studied if wetting properties from this functionalized glass slides could change by means of selective light exposure.

The goal of this work is, in essence, to study three different strategies for surface wetting modification:

- Through controlled degradation of surface monolayers to obtain specific wettability.
- By mixing two alkyilsilanes with different chain-length and therefore different wetting properties to obtain a functionalized glass slide with the desired water adhesion to the surface.
- Using photosensitive silanes to obtain a functionalized glass slide that can change its wetting properties when irradiated with specific wavelengths.

5. EXPERIMENTAL SECTION

5.1. CONTACT ANGLE

Contact angle measurements were taken using a custom-built goniometer (Fig. 3). 4µL drops of mili-Q water were placed over the surface using a micropipette. The fitting was made using a B-spline snake (active contours) method [26] on ImageJ. As different angles are obtained from the left and right sides of the drop, the average value was the one studied as contact angle. For each slide, three randomly placed drops were analysed to reduce error.

5.2. MONOLAYER DEGRADATION

5.2.1. Monolayer deposition

Several microscope glass slides (Duran Group, Germany) were functionalized with Dimethyloctadecyl [3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP), to study the influence that the monolayer degradation has over wetting properties.

Before functionalization, the glass slides were cleaned and activated at the same time using piranha solution [30% H_2O_2 (Sigma-Aldrich) and concentrated H_2SO_4 (PanReac) 1:3 v/v] until cooling. After piranha cleaning, the slides were rinsed with mili-Q water, dried with a N_2 stream and immediately immersed in the freshly prepared deposition solution. As DMOAP (Acros Organics) is soluble in water, a 0,01M solution was prepared in mili-Q water. The glass slides were immersed for 30 minutes at room temperature, then rinsed with purified water, dried with N_2 and heated at 130ºC during 1,5 hours [27].

5.2.2. UV degradation

The surface monolayer was degraded using the 250 nm emission band from a mercury lamp (USHIO USH-102D). It was coupled with a custom-made structure consisting of an opaque cylinder of variable length and a system that supported the glass (Fig. 7). Different exposure time and distances from the light source were studied. The degradation effect over the wetting properties of the glass slides was controlled though contact angle measurements taken before and after the UV treatment.

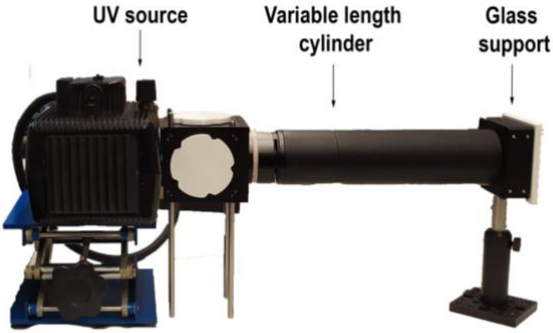


Fig. 7 Structure used for the UV degradation of the DMOAP monolayers on glass slides

5.2.3. Plasma degradation

A low-pressure Plasma system (Fig. 8) (Diener: Plasma-Surface-Technology. Zepto Model 2. 0 - 100 W) in O_2 atmosphere was used to degrade the surface monolayer. As the model allowed potency, time and, O_2 pressure control, these three parameters were studied to ensure soft degradation conditions. With potency below 9%, the plasma chamber did not illuminate so we assumed that it was the lower potency we could work with. O_2 pressure from 0,3 to 0,8 mbar were studied, as 0,3 was the lower pressure obtained with our vacuum system. To study the degradation effect, contact angle measurements were taken before and after the plasma treatment.

Fig. 8 Image of the low-pressure Plasma system used inside a fume hood (Left). When introducing O_2 to the chamber, the plasma colour changes form violet-blue to magenta, as shown in the image (right).

5.3. CHAIN LENGTH INFLUENCE

5.3.1. Mixed monolayer deposition (Glass)

Glass surfaces were functionalized with different ratios of C2 and C18 alkylsilanes. The SAMs were prepared according to published procedures for mixed monolayers deposition [3]. Microscope glass slides (Duran Group, Germany) were cleaned with piranha solution [30% H_2O_2 (Sigma-Aldrich) and concentrated H_2SO_4 (PanReac) 1:3 v/v] until cooling. After piranha cleaning, the slides were rinsed with mili-Q water, dried with a N_2 stream and immersed in toluene (Sharlau, reagent grade). A deposition solution of alkylsilanes and n-butylamine (Sigma-Aldrich) was prepared in toluene (Sharlau, reagent grade) at 3:1:200 volumetric ratio, respectively. The alkylsilanes used, n-octadecyltripethoxysylane (C18) (abcr GmbH, Germany) and triethoxy(ethyl)silane (C2) (Sigma Aldrich), were mixed at varying molar ratios: mol_{C18}/mol_{total} =

r_{C18} = 0, 0.1, 0.2, 0.5, 0.7, 1. After toluene, the glass slides were immediately immersed in the freshly prepared deposition solution and heated at 60ºC during 1h. Upon removal, the slides were rinsed with toluene, dried under a N_2 stream and stored at room temperature in a vacuum desiccator. Contact angle measurements were taken within 3 days.

5.3.2. Ellipsometry

SAMs thickness was studied using the spectroscopic ellipsometer Alpha-SE Ellipsometer (J. A. Woollman Co. Inc.) and CompleteEASE® software. Silica slides were functionalized using the "mixed monolayer deposition" procedure described in section 5.3.1.

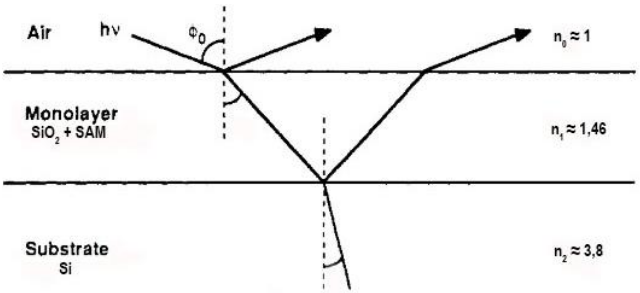


Fig. 9 Two-layer model used in ellipsometry *(Adapted with permission from* [28]. *Copyright 2020 American Chemical Society).*

Ellipsometry uses the refractive index of materials to relate polarization changes of reflected light with the layer thickness [29]. A two-layer model was considered for this study (Fig. 9). The measurements were taken with a wavelength of 632.8 nm with an incidence angle (from the normal to the plane) of 70°. The refractive index form CompleteEASE® software database ("Si.mat") was used for the Si substrate. An equal refractive index of 1,46 was assumed for SiO_2 and the mixed monolayer, as similar values have been used on different published works [3], [24]. SiO_2 refractive index is well known (1,46) [30]. Howeveer, a specific value for alkylsilanes self-assembled monolayers has not been defined. For their study, Wasserman et al. chose a refractive index of 1,45 for the monolayer, as previous reflectivity studies showed that the monolayer presented an electron density similar to that of bulk paraffin (1.42 - 1.44) [28]. Also, different values have been reported for crystalline alkylsilanes, which have refractive index of 1,37 for 1C [31] and increase when more carbon atoms were added to the alkyl chain. A value of 1,44 has

been reported for crystalline hexadecyltrialkoxysilane (C16) [32]. As we work with C18, it gives us more reasons to think that the 1,46 approximation is good enough.

The SiO_2 thickness was measured for each slide after piranha treatment and subtracted from the value of the functionalized substrate. The Si slides were cleaned after the measure with a low-pressure Plasma system (Diener: Plasma-Surface-Technology. Zepto Model 2. $70\%_{potency}$) in O_2 atmosphere (0,6-0,8 mbar) for 1 minute to reduce surface contamination and increase hydroxylation of the SiO_2 for better functionalization. Contact angle measures were taken after the ellipsometry study.

5.4. PHOTOSENSITIVE ALKYLSILANE

Glass slides were functionalized with a mixture of a photosensitive and a nonphotosensitive silane [(3-Aminopropyl)triethoxysilane, APTES]. The photosensitive compound was (E)-4-(4-((4-octylphenyl) diazenyl)phenoxy)-N-(3-(triethoxysilyl)propyl)butanamide (AZO), which was custom-synthesized by GalChimia, Spain. Its azo group (N=N) changes from trans to cis isomerization when irradiated with UV light. The process can be reversed with Blue light (Fig. 10).

The silanization was carried out following a published procedure [33]. Before the monolayer formation, the microscope glass slides (Duran Group, Germany) were cleaned with piranha solution [30% H_2O_2 (Sigma-Aldrich) and concentrated H_2SO_4 (PanReac) 1:3 v/v] until cooling, rinsed with mili-Q water, dried under a stream of N_2 and immersed in toluene (Scharlau, reagent grade). The deposition solution was prepared by dissolving the alkylsilanes with n-butylamine (Sigma-Aldrich) and toluene (Sharlau) at mass ratio 1:7:1730. Three different molar fractions of AZO/APTES where studied: $mol_{AZO}/mol_{total\ (AZO+APTES)} = r_{AZO}$ = 0.83, 0.30, 0.15. The glass slides in the deposition solution were heated at 80ºC for 2h. Upon removal, the they were rinsed sonicated for 5 minutes with toluene, dried with a stream of N_2 and stored at room temperature in a vacuum desiccator without light exposure.

A UV-Visible spectrum (UV-1800 Shimadzu UV spectrophotometer) of the glass slides was made before and after UV light radiation to ensure proper attachment of the photosensitive alkylsilane and to study the isomerization process. To place the glass sample in the spectrophotometer a custom made adapter was used.

Contact angle measurements at ambient-light and no-light conditions under red light were taken within 3 days from functionalization. Three cycles of “blue light exposure (5 min.) - contact

angle measurement - UV exposure (5min.) - contact angle measurement" were carried out for each glass slide.

Thorlabs LEDs M365LP1 365 nm (UV) and M455L4 455nm (Blue) were used. For each radiation, the glass slides were placed where the light power density on the sample surface was approximately 30 mW/cm^2 (UV) and 2 mW/cm^2 (Blue).

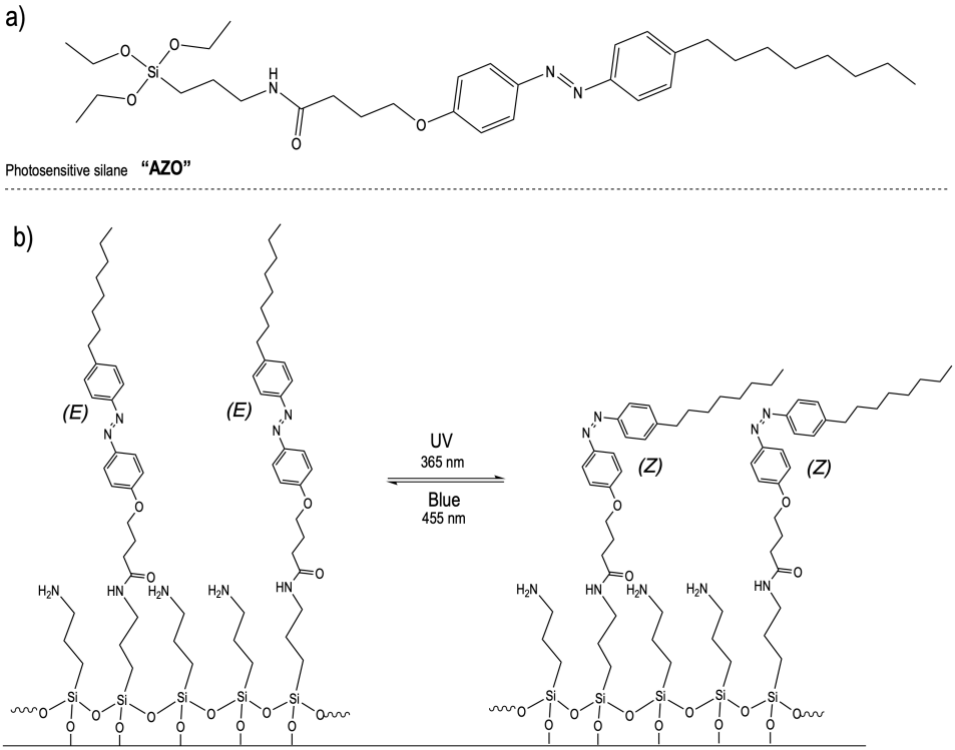


Fig. 10 a) Chemical formula of the AZO compound. b) *trans – cis* isomerization of the AZO compound

6. RESULTS AND DISCUSSION

6.1. DEGRADATION OF THE MONOLAYER

Contact angle measurements before and after exposure to the mercury lamp light were the same, so we concluded that no degradation took place (Fig. 11). The first slides were exposed to the UV light at a distance of approximately 40 cm for 1h. When no degradation was found, we reduced the distance to 10 cm (the minimum) to increase the light intensity. However, degradation was not found either.

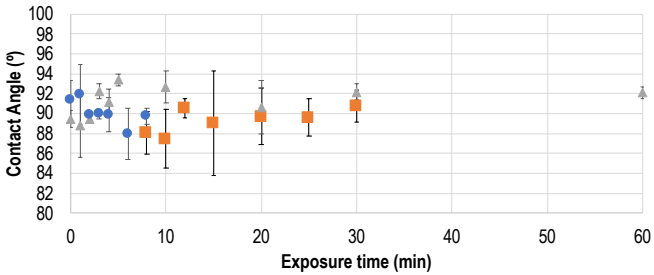


Fig. 11 Contact angle values for different exposure times at 10 cm form the light source. Different colours represent different glass slides. Error bars express the error within the three drops placed for the same slide. No difference was found.

Light sources have a specific lifespan after which its intensity is reduced. We worked with a light source that had already passed its maximum working hours. This, combined with the low intensity of the 250 nm band from mercury lamps (Appendix 2), gave us good reason to think that the degradation did not take place because we were not exposing the glass slides to 250 nm radiation. This could not be proved as we did not have a filter for this wavelength and therefore its intensity could not be measured.

Plasma treatment was found to be useful to eliminate the DMOAP monolayer but not to obtain a partial degradation. Even the softest conditions we could work with were too harsh and all the monolayer degraded (O_2 pressure = 0,3 mbar 10s treatment 9% potency). Contact angle measurements after the plasma treatment could not be measured; the drops spread over the surface the same way they did before functionalization (Fig. 12).

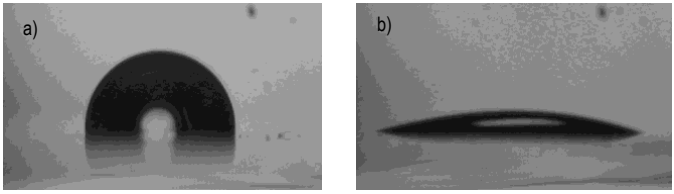


Fig. 12 Water drops placed before (a) and after (b) the softest plasma treatment conditions.

6.2. CHAIN LENGTH INFLUENCE

As expected, the contact angle of functionalized SiO_2 surfaces was higher than non-functionalized SiO_2, which is highly hydrophilic (high surface free energy) with values of 0º [34]. The contact angle values also increased with the amount of C18 present on the mixed monolayer, changing from hydrophilic to hydrophobic as shown in Fig. 13.

Water is a polar solvent that has strong hydrogen bonds in its structure, while the alkyl chains are nonpolar and cannot form hydrogen bonds. This leads to no adhesive forces between water and molecules form the SAM and, as a consequence, hydrophobicity of the glass slide when functionalized with alkyl chains.

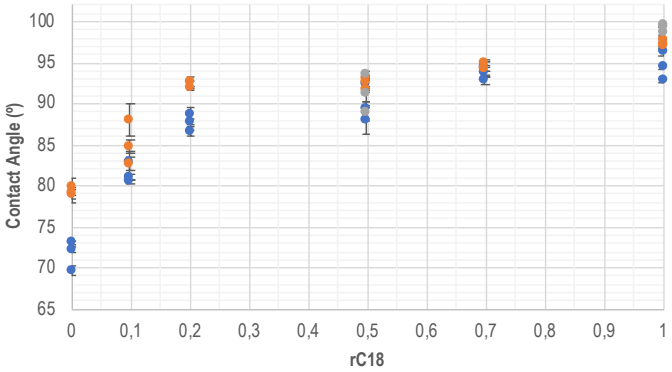


Fig. 13 Water contact angle on a C2/C18 mixed monolayer varying the C18 molar fraction. Values with the same colour and r_{18} are replicates form the same glass slide. The error bars express variability within the fitting of the same drop. If it does not appear for one value, the error is smaller than the size of the symbol

This influence that the chain-length has over the contact angle, has also been found on alkanethiols on Au, Ag, Cu. It has been demonstrated that van der Waals forces between the liquids and the metal do contribute significantly to contact angle when its distance is small enough (short alkanethiols C < 9). However, the van der Walls forces calculated for SAMs on SiO_2 could not explain its contact angle decrease [35]. It was concluded that the main reason for the decrease in the contact angle on short-chain alkylsilanes can be explained by changes in the SAMs structure.

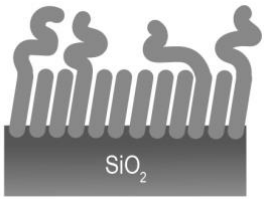


Fig. 14 Representation of the mixed monolayer structure.

AFM studies found that for shorter chains (C < 8) several uncovered SiO_2 areas could be found [36], leading to water contact with a highly hydrophilic surface and therefore lower contact angle.

Mixed monolayers of different chain-length molecules have two distinct regions: a densely packed layer in contact to the surface and an upper layer consisting of only the top portion of the longer chain alkylsilanes (Fig. 14). As there are fewer molecules in this upper layer its order decrease, exposing the polymethylene backbone of the alkysilanes and creating a mixture of -CH_3 and -CH_2- groups [37]. For low r_{C18} values, the C18 molecules are less likely to interact with each other and therefore more likely to expose its methylene groups to the surface. This reduces the contact angles, as -CH_2- has more water adhesin than -CH_3 [38].

Ellipsometry measurements are thought to be useful when characterizing the amount of C18 on the surface, as previous works demonstrated a relationship between chain-length and the monolayer thickness. Our results (Fig. 15) neither reflected the expected gradual increase of the monolayer thickness when increasing C18 molar fraction nor had the expected thickness for the pure monolayers (C2 = 7-9 Å / C18 = 17 - 20 Å) [3], [24]. Inaccuracy when characterizing the oxide thickness has been thought to be responsible for the erroneous values, dismissing the possibility of wrong attachment of the alkylsilanes as we have obtained similar contact angle results to those previously reported [3].

It has to be taken into account that we have used butylamine as a catalyst and prepared the monolayers at high temperatures. In this conditions covalent attachment should be expected and as a consequence monolayers thinner than the ones for fully stretched alkyl chain (section 3.2.2) [24].

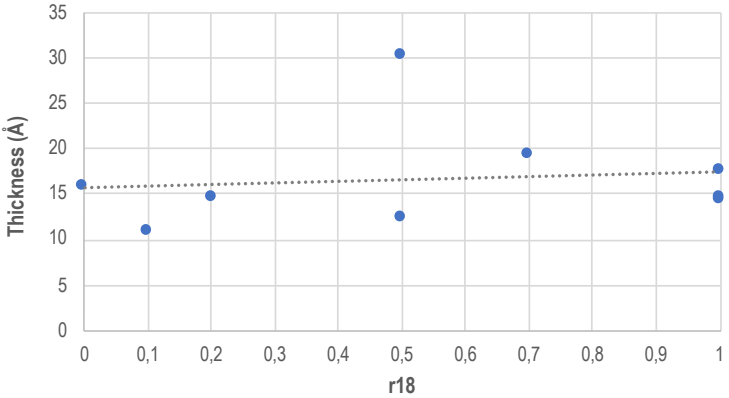


Fig. 15 Ellipsometric thickness of a C2/C18 mixed monolayer with varying the C18 molar fraction. Each symbol (•) represents one slide measurement. Error is smaller than the size of the symbol used so it does not appear. The dashed line represents a linear regression of the results. Statistically, the gradient was zero.

6.3. PHOTOSENSITIVE WETTING PROPERTIES

The spectroscopy analysis reassured proper attachment of the AZO silane into the glass slide as the spectre had its absorption peaks. After exposure to a wavelength of 455 nm, a high intensity peak in the UV zone appeared indicating that there were AZOs with the *trans* isomerization that absorbed a wavelength of approximately 350 nm when changing to *cis.* On the other hand, after exposure to UV light the peak at 350 nm disappeared, indicating that nearly all the molecules already had the *cis* structure. Instead, there was one peak at 450 nm, indicating that the *cis* isomers were changing to *trans* (Fig. 16*a*).

In addition, it was demonstrated that the different molar fractions in the deposition solution were reflected onto the glass slide, as higher molar fractions had higher peaks; there were more AZO on the glass slide who could absorb the wavelength (Fig. 16*b*).

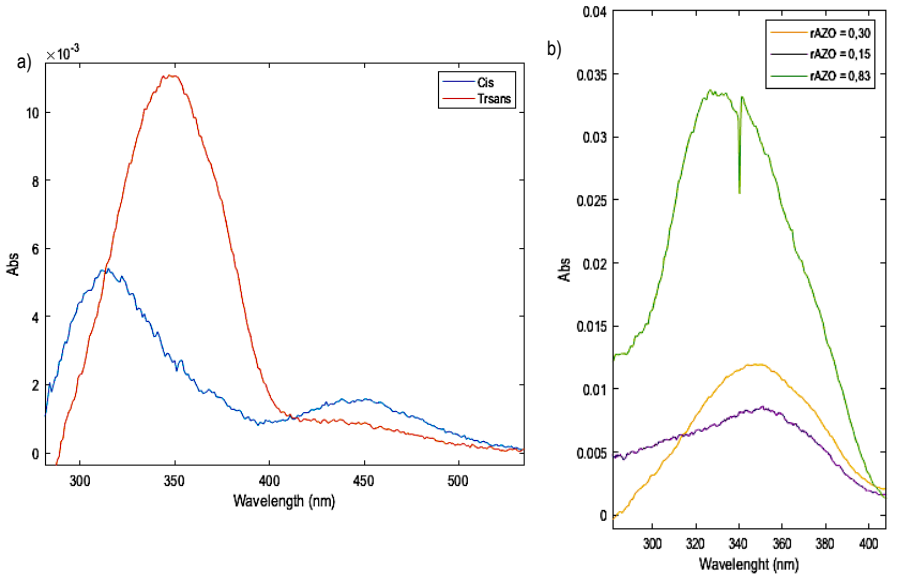


Fig. 16 Spectra of AZO functionalized glass slides. a) r_{AZO} = 0,30. Orange line "Trans" spectrum was made after 5 minutes irradiation with blue light (455 nm). Blue line "Cis" after 5 minutes irradiation with UV light (365 nm) b) influence of the deposition solution r_{AZO} over the amount of AZO on the glass slide.

At ambient light, no significant contact angle decrease for either of the molar fractions was obtained when changing from *trans* to *cis* (Fig. 17a). We studied the isomerization rate from *cis* to *trans* when the room light was on (Fig. 17b). After just 5 minutes the absorption peak of the *trans* isomer was already present, so it was thought that maybe the background blue wavelength in the room was enough to prevent the contact angle changes from being significant.

When making the measurements in dark conditions with red light, the contact angle of the glass slides decreased significantly after UV radiation (Fig. 18). The results from the three *trans-cis* cycles did not change for any of the molar fractions, which agreed with the spectroscopy analysis that the process is reversible.

It was expected that water affinity decreased when increasing the amount of AZO present on the surface, as there are more nonpolar -CH_n groups instead of the -NH_2 form APTES that can form hydrogen bonds and therefore increase water affinity. This trend was true for r_{AZO} 0,83 and 0,15, but r_{AZO} 0,83 had lower contact angles than r_{AZO} 0,15. The r_{AZO} 0,83 study was made in a different day so changes in ambient factors, such as temperature and humidity, are thought to have influenced the results. More replicates should be made to conclude if the expected

relationship between AZO molar fraction and water affinity is valid. Despite this, it has been proved for all the molar fractions that the induced *cis* isomerization increase adhesive forces between water and the surface.

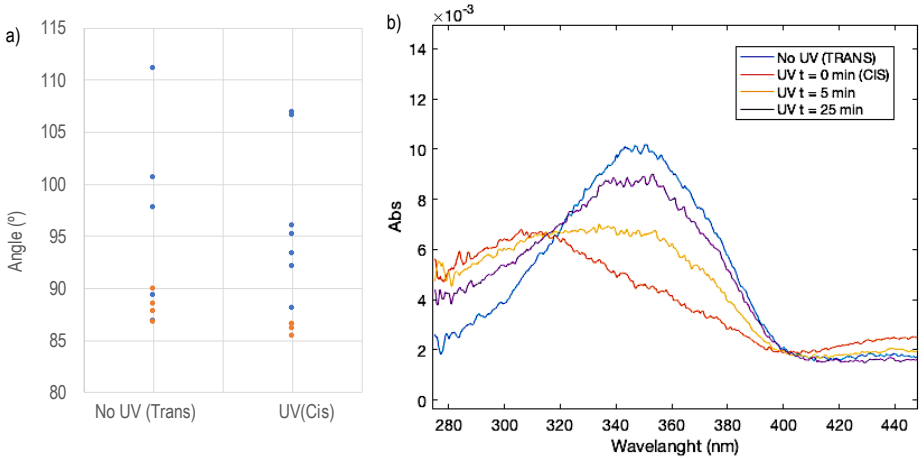
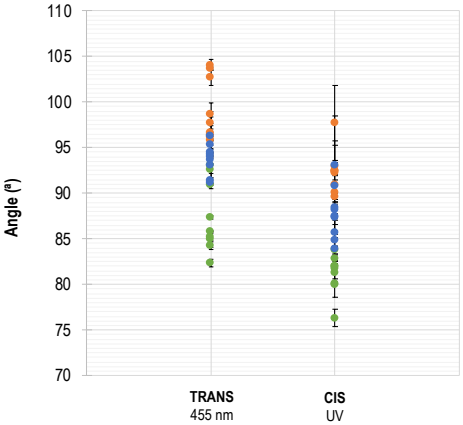


Fig. 17 a) Contact angle form the *trans* and *cis* isomer of the r_{AZO} 0,83 (Blue) and 0,15 (Orange). Ambient light conditions. Results from the first *trans* and *cis* cycle. No variation was found. b) *Cis*/*Trans* isomerization when absorbing ambient light. Blue: after exposure to 455 nm (Trans). Orange: After UV radiation (Cis) Yellow and purple: after 5 and 25 minutes exposure to ambient light.

As mentioned in 3.1.2, surface roughness enhances hydrophobicity and hydrophilicity, as more interactions in the solid-liquid interface take place [12]. As r_{AZO} 0,15 is the only slide that changes from hydrophobic to hydrophilic, a the coarse part of a microscope glass slide was functionalized using the same procedure to see if the contact angle change could be amplified. However, the difference between *cis* and *trans* remained the same (Fig. 18).

The *cis* isomer was theorised to decrees the contact angle as it exposes functional groups that can reduce the water surface tension by interacting with its molecules. The *cis* structure is smaller than the *trans,* so the isomerization approaches water to the amine groups of the APTES, which can form hydrogen bonds with the H_2O molecules. In addition, the N=N group of the AZO is exposed to the surface, instead of just the methyl and methylene groups, increasing the polarity of the molecule and as a consequence its water affinity. The amount of AZO on the surface should be optimized for grater changes in *trans-cis* contact angle, as many AZO on the surface might prevent them from property bending when changing form *trans* to *cis* and therefore not exposing the water-affinity groups.



	Trans	*Cis*
r_{AZO} **0,83**	99 ± 1 º	91± 1 º
r_{AZO} **0,30**	87,4 ± 0,7 º	81± 1 º
r_{AZO} **0,15**	93,7 ± 0,7 º	88 ± 1 º
Coars r_{AZO} **0,15**	100 ± 1 º	93 ± 2 º

Fig. 18 Contact angles after *trans* and *cis* isomerization under no light conditions. The error bars express variability within the fitting of the same drop. If it does not appear for one value, the error is smaller than the size of the symbol used.

It has been reported that SiO_2 functionalization at high temperatures and using amine as a catalyst can produce disordered structures (covalent attachment), instead of well-ordered assemblies of closely packed parallel molecules [24]. If the AZOs do not organize perpendicularly to the surface in a way that, when the cis isomerization takes place, the amount of amine groups form APTES exposed to water does not increase, the contact angle before and after UV radiation is expected to be the same. This disorder may have then reduced the contact angle difference between *trans* and *cis* if the isomerization of the all the AZO molecules did not expose different amounts of amine groups to the liquid. For further studies, it may be interesting to study glass slides functionalized without the catalyst and using lower reaction temperatures to see if the assembly order has an influence over the contact angle results.

7. CONCLUSIONS

It has been demonstrated that wetting properties of originally hydrophilic glass slides can be modified through surface functionalization with silanes, and that different methods can be used to obtain the desired water affinity.

The effectiveness of monolayer degradation as a means of wetting properties control could not be proved due to lack of proper equipment. On one hand, the UV source used is thought to not have enough intensity to degrade the organic compounds because it had already past its maximum working hours. It would be interesting to repeat the UV degradation study with another light source to prove if this was the problem. On the other hand, plasma treatment is extremely harsh so the degradation degree could not be controlled.

The results obtained from contact angle measurements of glass slides functionalized with different molar fractions of C2 and C18 alkylsilanes agree with published results: the water contact angle increased when increasing the amount of long-chain alkylsilane. If specific wetting properties are needed, using an optimized mixture could be a good solution.

Our study on the monolayer thickness through ellipsometry did not reflect the expected results. We thought that, as reported, when increasing the amount of C18 the monolayer thickness would also increase. No thickness difference was found in our monolayers. Ellipsometry is a sensible characterization method, so we believe that in our working conditions the error from characterizing the oxide layer was higher than the expected variation.

When working in no-light conditions, we obtained a difference in the contact angle values from before and after UV radiation (*trans* and *cis* isomerization). We believe that mixed monolayer of APTES and AZO, our custom-synthesized silane, could be used to create photosensitive glass surfaces with varying wetting properties. The obtained contact angle difference was not as big as expected so we did not obtain significant hydrophilic-hydrophobic changes. Different factors, such as AZO molar fraction and reaction conditions, could be optimized in future studies to increase the difference between the two isomerization states.

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APPENDICES

APPENDIX 1: PLASMA TREATMENT

When energy is supplied to matter, its state changes; it goes from solid to liquid and finally to gas. However, if the energy supply continues, the existing atomic structure disintegrates creating high-energy charged particles, which make up a "fifth" matter state known as **plasma**. It can be artificially created by heating a neutral gas or subjecting it to a strong electromagnetic field [1]. In this work, the low-pressure Plasma system (Diener: Plasma-Surface-Technology. Zepto Model 2) uses an electromagnetic field.

During plasma treatment, many processes take place simultaneously so the mechanisms behind its effect on materials are still unclear. Despite this, it has many different applications. In surface technology, this ionized gas can be used, among other things, for surface activation and cleaning.

Surface activation of SiO_2 :

Depending on the gases present on the atmosphere when creating the plasma, two processes can take place: introduction of chemical functionalities (plasma ions) to the surface or creation of free radicals that can introduce the functionalities in following steps. Plasma activation with gases that contain oxygen introduce oxygen-containing functional groups such as hydroxyl groups, carboxylic acid groups [2]. Activation of SiO_2 for functionalization with silanes consists of surface hydroxylation, so O_2 atmosphere should be used.

Surface cleaning:

Organic compounds, such as hydrocarbons, can be found in nearly all the surfaces. This organic compounds can be degraded using plasma treatment when UV radiation is formed. High-energy UV radiation divides macromolecules thought a process known as photolysis. The combination of UV radiation with oxidants, such as the O_3 that can be formed in the plasma environment, leads to photooxidation, another degradation mechanisms more effective than just UV. Oxygen radicals from the plasma and split-off hydrogen radicals join the macromolecules fragments forming H_2O and CO_2 as final products [3].

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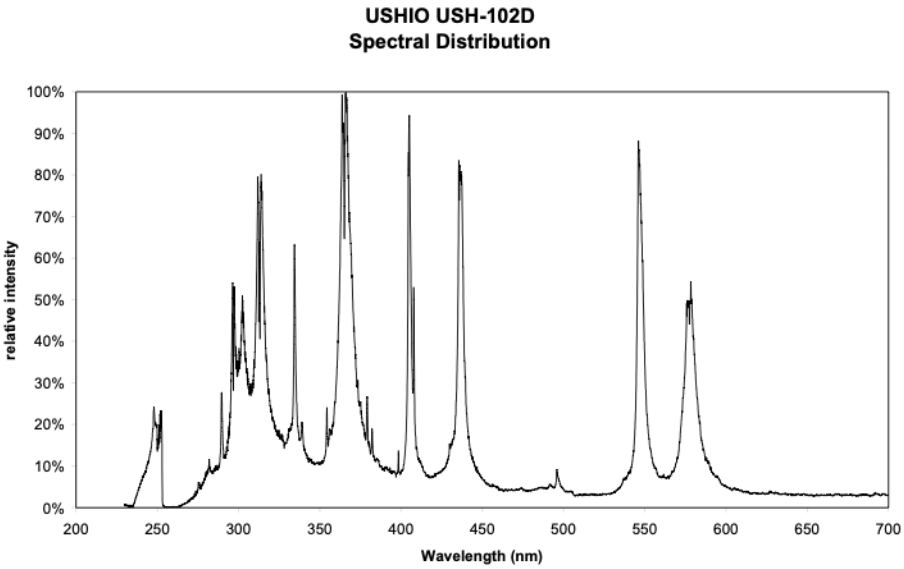
APPENDIX 2: MERCURY LAMP SPECTRAL DISTRIBUTION



"Lamparas y baterias medicas" (2017) [Online]. Available: http://www.lamparasybateriasmedicas.com/wp-content/uploads/2017/12/USH-102D_Spectral_distribution.pdf